

First-principles study of diffusion of constituent atom in CuInSe_2

Satoshi Nakamura, Tsuyoshi Maeda, and Takahiro Wada

Department of Materials Chemistry, Ryukoku University
1-5, Yokotani, Oe-cho, Seta, Otsu, Shiga, 520-2194, Japan
Phone: +81-77-543-7468 E-mail: t10d003@mail.ryukoku.ac.jp

1. Introduction

Cu(In,Ga)Se_2 (CIGS) is among the most promising materials for thin film solar cells. Excellent radiation tolerance of the CIGS solar cells has been reported by some groups [1]. A research group at the Japan Aerospace Exploration Agency, JAXA, demonstrated high radiation tolerance of CIGS solar cells in space by monitoring their performance on Mission Demonstration test Satellite-1 (MDS-1) [2]. Short-circuit current of the CIGS solar cells did not degrade, and open-circuit voltage of the cells degraded only about 1%. Researchers found high recovery from radiation damage of CIGS solar cells due to thermal annealing from a ground test. They also reported that the recovery rate of CIGS solar cells depended on the annealing temperatures. The radiation defect in CIGS solar cells, which caused their performance to decline, was caused by various defects in CIGS crystals. Cu-related defects formed more easily than In-, Ga- and Se-related defects [3]. The Cu-related defects, such as Cu vacancy, V_{Cu} , and Cu-related complex defect, $(2V_{\text{Cu}}+\text{In}_{\text{Cu}})$, were stable in CuInSe_2 (CIS) crystal [4, 5]. The degraded photovoltaic performance in CIGS solar cells was recovered by atomic migration of constituent atoms, Cu and In, during thermal annealing. A European research group reported that Cu migration effects were reversible and their possible detrimental effects were eclipsed by the beneficial effect of the metastable states [6]. However, there are few reports of migration of constituent atoms in CIS crystal. In this paper, we study the migration of the Cu in CIS crystal by first principles calculation within a density functional theory.

2. Computational Procedures

2.1 Structural optimization of CuInSe_2

We performed first-principles calculations within a density functional theory as implemented in the program package Dmol³ [7]. Electron exchange and correlation functional employed the GGA-PBE functional. We performed all-electron scalar relativistic calculations. The wave functions were expanded in terms of a double-numerical quality localized basis set with a real-space cutoff of 5 Å. For primitive cells of CIS, a $5 \times 5 \times 6$ k point mesh generated by the Monkhorst-Pack scheme was employed for numerical integrations over the Brillouin Zone. The initial structure of CIS adopted as the experimental one was obtained from the Inorganic Crystal Structure Database (ICSD). We optimized lattice parameters a and c , and the u -parameter of the Se atom, $u(\text{Se})$, through the minimization of total energy. A Cu diffusion model was constructed of a supercell with 64 atoms, which was 4 times greater

than that of the chalcopyrite-type unit cell. We introduced a point defect of Cu vacancy in the supercell because Cu vacancy was the dominant defect in CIS thin film, and the formation energy of Cu vacancy was a negative value [4]. Atomic arrangements were fully relaxed, while residual forces for all atoms were less than 0.002 Ha/Å.

2.2 Modeling of Cu diffusions in CuInSe_2

Figure 1 (a) shows the initial structure for the Cu diffusion model in a supercell of CIS, which was 4 times greater than that of the chalcopyrite-type unit cell. The initial structure has a Cu vacancy at (0.5, 0.75, 0.75). The Cu atom at (0.5, 0.5, 0.5) moves to a vacancy site at (0.5, 0.75, 0.75). Finally, the Cu atom occupies the (0.5, 0.75, 0.75) site and leaves the vacancy at (0.5, 0.5, 0.5). The final structure is shown in Fig. 1 (b).

We performed the linear (LST) and quadratic synchronous transit methods (QST) combined with conjugate gradient method (CG) refinements to obtain the transition state [8]. LST gave the maximum pathway along the linear synchronous transit path between the initial and finite structures. The CG method provided the saddle point of potential surface from the energy maximum of the LST pathway, and QST allowed the maximum pathway along the quadratic synchronous transit path through the saddle point. The refinements were repeated until the transition states as the stationary saddle point was located. The root mean square convergence of gradients was less than 0.002 Ha/Å. The nudged elastic band (NEB) method [9] was performed to find the minimum energy path between the initial and finite structures by configured intermediate images, and those images were connected by springs to each other. We employed convergence of gradients of less than 0.002 Ha/Å.

3. Results and discussion

Four processes were considered for the migration of Cu at the regular site at (0.5, 0.5, 0.5) to the vacancy site at (0.5, 0.75, 0.75). In the first process, Cu atom passed near the three-coordinated Se atoms at (0.460, 0.535, 0.540). In the second process, Cu passed near the centers of the octahedral site of the CIS lattice at (0.375, 0.625, 0.625). The third and fourth processes were similar to the first and second processes; the Cu moved to the Cu vacancy through the three-coordinated Se atoms along the migration path. The lowest activation energy of Cu migration was obtained for the second process, and there was migration of Cu atom near the center of the octahedral site of the CIS lattice. The calculated activation energy of Cu migration is 1.17 eV.

Figure 2 shows the local atomic geometry of the transition state of Cu migration. In the transition state, Cu atom is

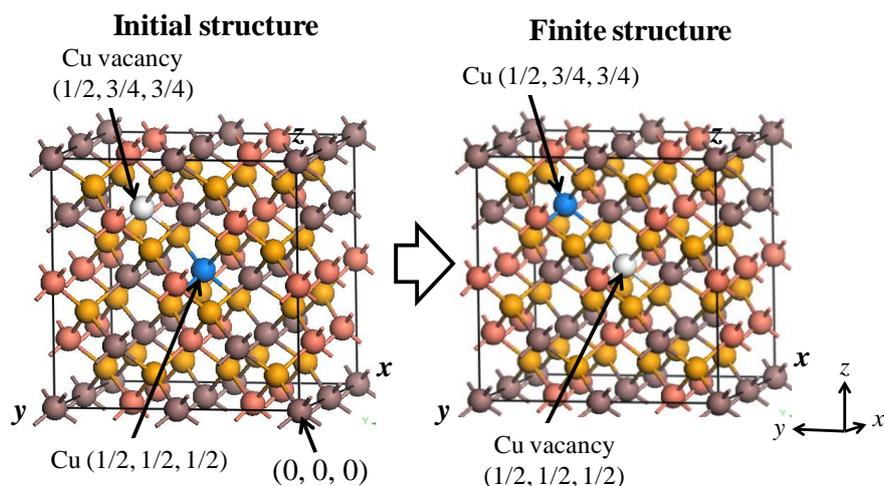


Figure 1. Cu diffusion model of initial structure (a) and finite structure (b) in CuInSe_2

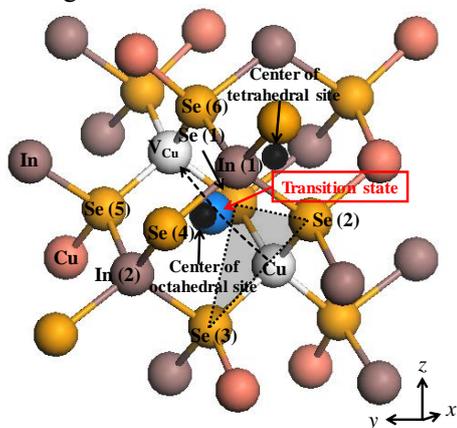


Figure 2. Local atomic geometry of transition state of Cu migration

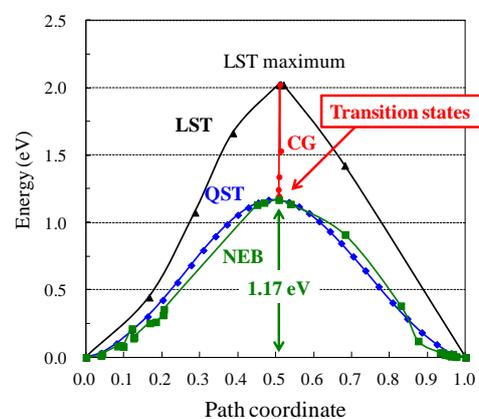


Figure 3. Energy along Cu migration path

located at $(0.431, 0.628, 0.626)$, which is near the center of the octahedral site of the CIS lattice $(0.375, 0.625, 0.625)$. We also calculated activation energy of Cu migration via the tetrahedral site of the CIS lattice. The obtained activation energy of Cu migration via the tetrahedral site of the CIS lattice was 1.23 eV, which was higher than that via the octahedral site. Therefore, Cu migration via the tetrahedral site occurs rarely.

Figure 3 shows the energy of the Cu migration pathway in CIS. The migration path of the Cu atom is located on the $(0 -1 0)$ plane. The total energy of the initial structure is set to 0 eV. The energy of LST maximum is 2.02 eV in the LST path, and the transition state is relaxed by the CG method. Finally, the obtained minimum theoretical activation energy is 1.17 eV. This value agrees with the experimental value (1.05 eV) for the activation energy of the recovery rate of the proton irradiation defect in CIGS thin film solar cells [10].

We also studied the migration of In atom in CIS crystal by similar first-principles calculation. The obtained minimum activation energy was 1.71 eV, which was much higher than that of migration of Cu. The result was consistent with our previous report [11].

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